Chapter 3
Polymeric Nanocomposite Membranes for Treatment of Industrial Effluents

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1 Introduction

Since the origin of this earth, all organisms including mankind are dependent on water. However, the progress of lifestyle, advancement in science and technology, and growing industries have led to an unfair distribution of the very limited fresh water sources among various segments of society. Millions of people mostly in developing and underdeveloped countries do not have access to potable water [1]. Moreover, the generation of large volumes of wastewater is unavoidable with the escalating demand for water in the industrial, agricultural, and domestic sectors. To compensate for this water scarcity, the used water must be treated, replenished, and reclaimed thereby fulfilling the water usage necessities of the ever-increasing population. Hence, the cost of freshwater generation has constantly been on the path of an upsurge. Water filtration has become a multi-billion-dollar industry that is

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A. K. Nadda et al. (eds.), *Membranes for Water Treatment and Remediation*,
Materials Horizons: From Nature to Nanomaterials,
https://doi.org/10.1007/978-981-19-9176-9_3

only growing with the alarming concerns about contaminants in water and decline in safety and cleanliness in easily available existing water resources. Membrane technology, though not a new technique, has emerged with extensive application in water treatment and desalination for domestic as well as industrial water supply and effluent treatment. Various water treatment facilities use membrane separation and membrane filtration including membrane-based hybrid technologies to clean surface water, groundwater, and wastewater in order to produce safe and hygienic water for drinking domestic and industrial use. This chapter gives an overview of the membrane process used for water remediation highlighting the employment of various polymeric membranes for the same along with existing challenges, emerging approaches, and future prospects.

2 Membrane Technology for Water Remediation

Membrane technology is a broad term that encompasses a wide range of scientific and engineering approaches for characteristic separation processes in various fields. The common factor in these processes is the use of a thin membrane for the separation of gas or liquid streams [2]. Membrane separation can be achieved via rejection or transportation of substances, components, chemical or microbial species through a semi-permeable or selectively permeable membrane. Owing to its multi-disciplinary characters, the capability of producing high-quality products and agility in system designing, membrane technology, has wide application in various industries such as food processing, bioprocessing separation, refining, and purification of products of pharmaceutical, biotechnological, beverages, food, metallurgy industries including water treatment [3].

Some of the advantageous features of the membrane separation process which often brands it as more preferred and suitable towards water treatment in comparison to other conventional methods are listed below:

- Clean technology
- Low energy consumption
- Continuous separation at mild operating conditions
- Possibility of adjustable membrane properties
- Leeway of hybrid processing with other techniques
- Easy upscaling

Membrane Separation, therefore, has the potential to give strong competition to the various existing water remediation processes and can easily replace conventional methods, such as chemical treatment processes, distillation, filtration, ion exchange, etc. [4]. However, just like any other process, membrane separation has its demerits such as concentration polarization, low selectivity, flux, membrane lifetime, and membrane fouling. Studies are being conducted to overcome these challenges, more about the challenges and the advanced and emerging approaches to tackle them have been discussed in Sects. 3 and 5 below.

2.1 Types of Membrane Process in Water Remediation

As mentioned above membrane process can have different approaches towards the separation of molecules and particles. Based on the different types of driving forces the process of movement of media through a membrane can be categorized as follows:

- Equilibrium based membrane processes
- Non-equilibrium-based membrane processes
- Pressure driven process and
- Non-pressure driven processes

The pressure-driven membrane processes also known as membrane filtration are the most widely accepted and employed membrane processes in the field of water treatment [5]. These processes can concentrate or separate pollutants by means of hydraulic pressure applied with filters with different pore sizes.

2.1.1 Pressure Driven Membrane Filtration

Membrane filtration is a characteristic pressure-driven separation technique that applies a membrane for mechanical and chemical filtering of particles and molecules of various sizes. The membrane filtration process has different levels based on their pore sizes and hence can be classified as microfiltration (MF), ultrafiltration (UF), nano filtration (NF), and reverse osmosis (RO) [2] as depicted in Fig. 1.

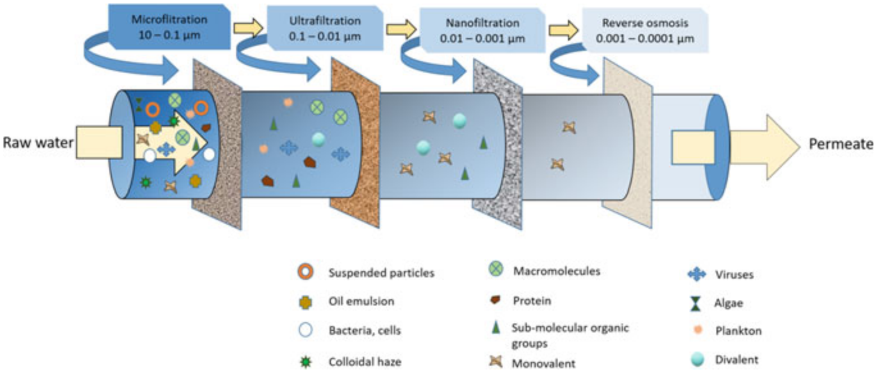

Fig. 1 Types of membrane filtration based on pore size

Microfiltration

Microfiltration is a low-pressure-driven separation process applied to eliminate particles with an average molecular weight of 400 k Dalton. The pore size of a microfiltration membrane ranges from 0.1 to 1.0 μm. It is mostly applied for concentrating and separating macromolecules, suspended particles, and colloids from an aqueous solution [6]. Microfiltration filters membranes are usually made of organic materials, such as various polymers like poly-ethylsulfone and polypropylene. It can also be made of inorganic materials, such as ceramic, glass, or sintered metal membranes [7].

Ultrafiltration

Ultrafiltration (UF) is a pressure-driven technique that applies hydrostatic pressure and concentration gradient to force water through a semi-permeable membrane, thereby leading to the separation of particles ranging from 0.1 to 0.01 μm. UF has gained wide acceptance and popularity owing to its capability to remove upto 100% pathogens including viruses and bacteria, most organic materials, particulates, even various salts, and low molecular weight particles. Therefore, nowadays "molecular weight cut-off" (MWCO) is best used to describe a UF membrane. MWCO is referred to the specific molecular weight at which upto 90% of the molecules are retained by a UF membrane. The UF technology is commonly applied for secondary and tertiary filtration stages in water treatment facilities, different industries such as food and beverage, paper pulp mill, etc. for removing turbidity causing particles and recycling of wastewater.

Nanofiltration

Nanofiltration (NF) is another pressure-driven membrane tool used for removing solutes and ionic molecules with a molecular weight typically ranging from 200 to 1000 g mol^{-1}. The pore size of NF membranes is typically on the scale of 1–10 nm and are employed to remove microbes, turbidity, the fraction of dissolved salts, and hardness. The application of NF membranes has been extended to the separation of molecules from organic solvents [8], and hence has a great potential in the refining and pharmaceutical industries. When it comes to the treatment of water NFs can be easily applied for cleaning surface water, groundwater, wastewater, and pretreatment for desalination as well. It is also used in the production of drinking water [9].

Reverse Osmosis

Reverse Osmosis or RO technology is one of the most powerful tools for water purification. In RO water purification systems, hydraulic pressure is applied to overcome the osmotic pressure thus forcing the solvent from a region of high solute concentration to a region of low solute concentration through a partially permeable membrane and hence the name reverse osmosis. This results in the retention of ions or large molecules on the pressurized side whereas the smaller solvent molecules freely pass through the membrane and are collected downstream. The pore size of the RO membranes can vary depending on the desired production rate for pure water on a daily or even an hourly basis. The commonly used RO membranes are generally composed of semi-permeable polymeric ultra-thin films made of polyamides, polysulfones, cellulose acetate, etc. RO technology is extensively used in drinking water purification systems, large-scale production of potable water, sea water desalination, in industrial sectors for removal of suspended as well as dissolved solids and microorganisms [10].

2.1.2 Non-pressure Driven-Forward Osmosis

When Forward Osmosis or FO is defined as a non-pressure driven process, it implies that FO does not require hydraulic pressure gradient, instead, it occurs with the help of natural osmotic pressure along a concentration gradient. When the osmotic pressure gradient between the feed and draw solutions is positive and has the same hydrostatic pressure, the water is forced through the membrane from the feed to draw the solution while the contaminants are retained in the feed stream [11]. FO is widely applied for product concentration in food and beverages industries, for wastewater concentration facilitating zero-liquid-discharge-waste disposal. In FO-based hybrid techniques for water treatment, FO is often applied as a pre-treatment footstep, while RO and NF are used for water recovery and regeneration [12]. FO is also emerging as a potential applicant for direct desalination of seawater [13].

3 Polymers: Ideal Material for Membrane Fabrication

The functional element of any membrane filtration system is the membrane. Membranes can be prepared from organic or inorganic materials. Ceramics, zeolite, sintered metals, and oxides such as silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), zirconia (ZrO_2), etc. are common examples of inorganic membranes used for water filtration [14]. While the organic materials used for membranes are mostly carbon-based and polymeric in nature, polymeric membranes have some leverage over inorganic membranes and therefore are the most preferred option for the membrane material. The advantages of a polymer as a suitable material for the membrane are shown in Fig. 2.

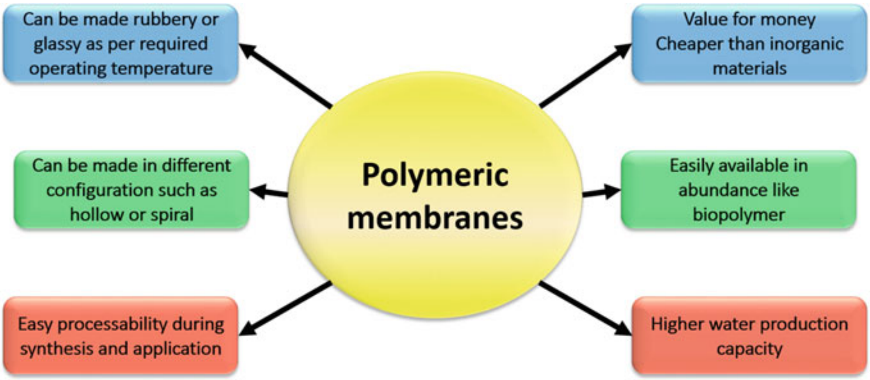

Fig. 2 Advantages offered by a polymeric membrane for water purification application

As polymeric materials are more flexible and easier to handle, it is often the first choice for preparing a membrane for filtration. Various polymers are applied as the functional membranous layer in all types of filtration methods mentioned above, namely MF, NF, UF, and RO. Some of the most common polymers that are potentially applied for membrane filtration are cellulose acetate, polyamide (PA), polysulfone (PS), polyethersulfone (PES), polyvinylidene fluoride (PVDF), polyvinyl chloride (PVC), polyvinyl alcohol (PVA), polyethylene glycol (PEG), polyacrylonitrile (PAN), polymethacrylic acid (PMAA) and polyaniline nanoparticles (PANI). However, polyethersulfone amide (PESA) is a new addition to the above list and there are many more polymeric materials that are being explored for their potential as a membrane candidate [15]. The nature of the polymer being used in membrane filtration is very critical as it plays the most significant role in determining the quality of the permeate generated and the overall cost of production of water. Appropriate selection of the polymer for a specific type of membrane filtration can ensure overcoming some major challenges such as the need for frequent membrane replacement and excessive energy consumption.

For enhanced performance, the polymeric membranes are often modified either chemically or by the addition of inorganic additives or blended with another suitable polymer. For instance, in order to achieve better strength in a highly porous membrane, polyvinylidene fluoride PVDF matrix was reinforced with polytetrafluoroethylene (PTFE) particles thereby reducing surface tension and increasing contact angle resulting in narrow pore size distribution and hence better strength [16]. The introduction of inorganic additives such as TiO_2 or SiO_2 helps improve hydrophobicity. Hydroxyl-rich silica particles were incorporated in a PVDF flat-sheet membrane to regulate its porosity and pore size. With increasing silica content, lower permeate flux, and a reduced rate of mass transfer between solvent and non-solvent was achieved. Moreover, the contact angle of PVDF was also increased [17]. Another successful way of enhancing membrane hydrophobicity is the addition of perfluorinated polymers. Blending perfluorinated polymers to PVDF or application of copolymers such as poly vinylidene fluoride-co-hexafluoropropylene PVDF-HFP can offer to be potential base materials for desalination membranes [18]. The incorporation of the hexafluoropropylene (HFP) monomer in the PVDF backbone resulted in lower crystallinity which in turn considerably enhanced the amorphous phase content [19].

3.1 Polymers for MF

MF membranes are generally applied for membrane distillation (MD), MBRs, OMBRs, and wastewater treatment. The integration of TiO_2 in MF membranes has emerged as a viable membrane separation technique. PES and PVDF membranes incorporated with were TiO_2 nanoparticles show a decrease in membrane porosity and an additional capability to degrade various pollutants like textile dyes, pharmaceutical compounds, and pesticides [20]. Although MD is easy to implement it has not yet achieved popularity at an industrial scale due to the major issues of MF membrane fouling and low flux. Recently studies have shown that surface modification of DCMD membranes by tetrafluoromethane (CF4) plasma resulted in a superhydrophobic membrane with increased flux and high salt rejection as compared to the virgin membrane [21]. Other studies have indicated that the introduction of grapheme oxide (GO) in MF membranes can effectively reduce membrane fouling. Owing to its hydrophilic nature and high negative zeta-potential arising from its functional groups, it can augment permeation through the membrane and obstruct fouling by reducing microbial biofilm formation [22].

3.2 Polymers for UF

PS, PES, PSF PEG are the polymers broadly employed for UF membranes. Although PS and PES have good mechanical properties, strong chemical stability, and a wide range of pH operations, their applications are imitated due to their hydrophobicity [23]. Most other polymers such as PVDF, PVC, and PMAA used in UF membranes throw challenges by being naturally hydrophobic. This can result in a decline of flux and buildup of organic materials favoring microbial growth followed and fouling and membrane failure subsequently. Hence modification of the membrane to increase surface hydrophilicity becomes necessary [24]. Reports from the past and recent studies have shown that the addition of nano-structured inorganic particles has helped reduce hydrophobicity by increasing surface hydrophilicity and flux rate [25]. The terminal silanol (Si–OH) groups on mesoporous silica particles (MSP-1) were reported to induce hydrophilicity in polysulfone PSF membranes [26]. Grafting of (2-hydroxyethyl methacrylate) (P(HEMA)) on TiO_2 nanoparticles followed by impregnation into PSF membranes reportedly showed superior hydrophilicity along with elevated flux rate and better antifouling properties when compared with pristine

PSF and TiO_2 [11]. Another study showed that coating PVDF UF membrane with dopamine solution facilitated the attachment and homogenous distribution of TiO_2 particles on its surface. This significantly improved hydrophilicity resulted in high flux and low fouling ratio [27].

3.3 Polymers for NF

Most NF membranes are composed of PI, PA, PVA, and PAN polymers. PI membranes show instability in polar solvents, chlorinated solvents, and in the presence of strong amines and strong acids or bases. Modification of such membranes via cross-linking is opted to increase chemical resistance. Poly-arylene ether ketone (PAEK) is another polymer suitable for NF membranes as it has high resistant to various solvents and strong acids and bases owing to its low degree of sulfonation. However, (PAEK) has a low permeability hence its separation performance was subjected to testing in dimethylformamide (DMF) and tetrahydrofuran (THF), and improved results were obtained [28]. A Polyamide NF membrane with a high level of pore size uniformity for the separation of sub angstrom scale molecules was prepared. The angstrom scale pore size was achieved by surfactant-assembly regulated interfacial polymerization (SARIP). The self-assembled surfactant network aided in faster and homogeneous dispersion of amine monomers on the solvent interface during polymerization, thereby producing an active layer of polyamide with consistent and precise sub-nanometre, angstrom scale pores [29].

3.4 Polymers for RO

As discussed, earlier RO is so far the best and most widely accepted technology for producing potable water. The most common polymers used for RO membranes are cellulose acetate (CA) and polyamide (PA). CA is opted for its natural availability and biodegradability, though PA is preferred due to its capability of stable performance under a wide range of pH as well as high temperatures. However, PA is susceptible to chlorine attack due to its amine group, which needs to be prevented by an additional de-chlorination step [30]. To avoid this issue of chorine attack any additional step, copolymers such as poly-arylene ether sulfone (PAES) which are resistant to chlorine attack due to the absence of any susceptible amide linkage are also widely used as RO membranes [31]. Disulfonated PAES co-polymer thin films were synthesized with a controlled degree of sulfonation and molecular weight achieved by the application of Meta-aminophenol. This was followed by further reaction with acryloyl chloride to attain acrylamide terminated PAES oligomers, which were then subjected to UV radiation for cross-linking. The final copolymer thin film was seen to have a smooth surface thereby encouraging high water passage and relatively reduced uptake and swelling [32]. In a recent study, the PA membrane for RO was modified with GO and poly acrylic acid (PAA) to enhance antifouling and anti-scaling properties. The resultant PAA modified GO coated RO membrane exhibited improved hydrophilicity and surface smoothness with a mere reduction of permeate flux by only 3%.

3.5 Nanocomposite Membranes

Polymer-based nano-composite membranes are chemically engineered materials which often contain target specific nanoparticles dispersed in the membrane matrix. Such nanocomposite membranes are extensively used for water treatment, solvent nano filtration, gas separation and many other operations. The type of nano fillers or nano particles used in nanocomposite membranes can be organic, inorganic, biomaterial or even a hybrid component. As per the requirement, the configuration of the nanocomposite membrane can be a flat sheet like or hollow fiber type. Based on the preparation technique the nanocomposite membranes can be classified into two major categories that are thin film nanocomposites and blended nanocomposite membranes.

3.5.1 Thin Film Polymer Nanocomposite Membranes

Thin film polymer nanocomposite membranes or TFC are achieved by either direct deposition of the nanoparticles on the membrane surface or by encapsulation of the nanoparticles within the membrane via interfacial polymerization. Direct deposition can be done by dip coating method where the nanoparticles self assemble to form a thin film on the surface of the membrane, or nanoparticles can be introduced onto a prepared membrane surface by pressure application [33]. Graphene oxide, silica, zeolite, silver, carbon nanotubes, titanium dioxide, are some common nanoparticles that are used as fillers in TFC membranes. Such membranes with nanoparticle incorporation offer various advantages such as high thermal stability, mechanical strength, selective permeability, hydrophilicity and resistance to extreme pH levels etc. However leakage of nanoparticles during high pressure filtration may become a challenge, but that too can be overcome by chemically modifying the particles to facilitate surface functionalization [34]. Hence such TFC membranes have gained high interest among researchers as well as industrialists. Fabrication of Polyethersulfone (PES) based thin film membrane with surface coated TiO_2 nanoparticles using PVA and glutaraldehyde as additives were reported in a recent study [35].

3.5.2 Blended Polymer Nanocomposite Membranes

In this type of membrane preparation nanoparticles are first mixed with polymer and dispersed in the casting solution before the membrane is casted. Such membranes are hence commonly called nanoparticles entrapped membranes. In this method the homogeneous dispersion of nanoparticles in the polymer matrix is an important factor. Agglomeration of nanoparticles is a common issue observed during the fabrication of nanoparticle entrapped membranes. This problem mainly arises due to the incompatibility between the inorganic and organic components, where interfacial tension also plays a major role in dispersion. These issues can cumulatively result in improper or heterogenous dispersion of the nanoparticles in the polymer matrix thus causing agglomeration. Application of dispersion agents to bind the inorganic nanoparticles to the organic polymer matrix is one way of overcoming this issue. Another technique to play down the agglomeration challenge is the surface modification and functionalization of the nanoparticles [34]. Jafar et al. prepared a TiO_2 nanoparticle entrapped PES membrane by dissolving TiO_2 in DMAc using PVP as additive [35].

4 Preparation Approaches Towards PM

Various techniques are applied for the preparation of polymeric membranes as well as the polymeric nanocomposite membranes. Some popular methods are discussed below.

4.1 Electrospinning

Electrospinning works on the basic principle of movement of liquid under the influence of electrostatic field forming nanofibres. This phenomenon was first observed by William Gilbert in 600. Since then, this electrohydrodynamic technique has evolved over the years to become the cheapest and most hassle-free method for the fabrication of nanofibers without self-assembly [36]. Electrospinning was first commercialized by application in air filters.

The electrospinning apparatus involves the use of a syringe in which the polymeric solution to be electrospun is poured. The syringe is suspended upside-down, and a metallic collector is laid under it. Subsequently, a high electric field is created between the syringe and the collector by charging the polymeric solution through the application of high voltage on it. This results in the formation of a droplet in the tip of the syringe. As the applied voltage becomes strong enough to overcome the surface tension of the droplet, it converts into a jet forming the ‘Taylor cone’. While the jet progresses towards the collector plate, it endures bending instabilities along with the evaporation of the solvent. This results in the formation of fibrils with a smaller diameter and longer length [37]. The nonwoven fibers are assembled in the collector plate (Fig. 3).

Yin et al. [38], synthesized sulfonated polyethersulfone nanofibrous membrane through the process of electrospinning. The pore size and distribution were

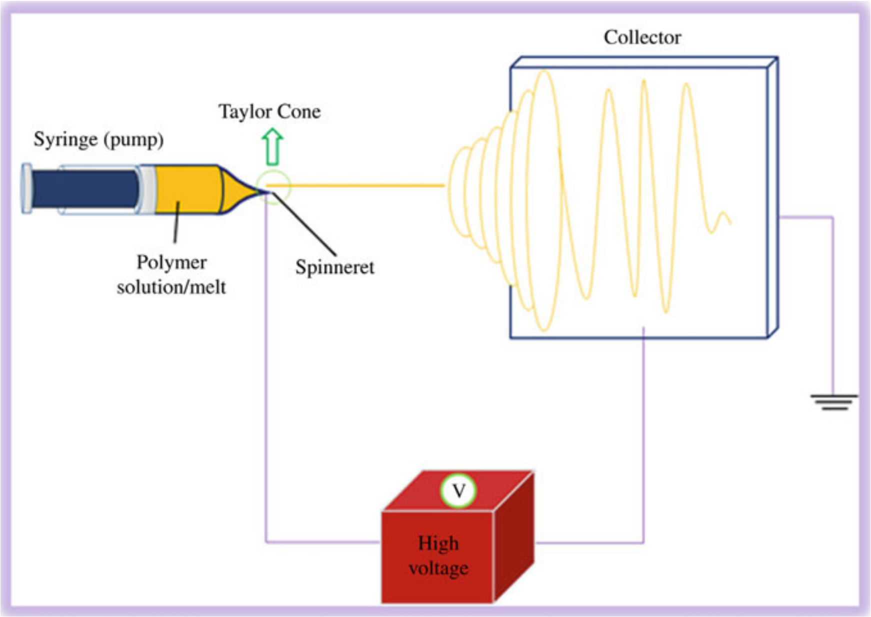

Fig. 3 Schematic representation of electrospinning technique. Reproduced with permission from Orasugh et al. [39], Elsevier

immensely influenced by the diameter of the fiber which in turn affects the adsorption of dyes and heavy metals. The membrane exhibited a flux of 320 L/m^{2}h against nanoparticles, methylene blue, and Pb (II).

4.2 Track Etching

The track etching technology involves the use of nuclear tracks for the fabrication of porous membranes. Polycarbonate track membranes were first commercialized in the 1970s.

There are a few methods to generate tracks in foils in order to transform them into porous membranes. Latent tracks can be produced by irradiating fragments from the fission of heavy nuclei on the film. A collimator is generally used in this process. Particles penetrating the film may rupture the polymer chain leaving behind damaged tracks. Another method involves the use of ion beams from accelerators. The damaged areas of latent tracks are eradicated and converted into hollow channels by the method of chemical etching [40].

Korolkov et al. [41] prepared poly(ethylene terephthalate) (PET) track-etched membranes and modified them by soaking in trichloro(octyl)silane for ameliorating its hydrophobic nature. The membrane was used for the separation of oil–water emulsion where chloroform–water and cetane–water were used as models for testing. Membranes having a pore diameter of 350 nm exhibited flux of 305 and 75 mL/m^2 h for chloroform–water and cetane–water respectively. Yeszhanov et al. [42] synthesized hydrophobic track-etched membranes by graft polymerization of triethoxyvinylsilane and covalent binding with perfluorododecyltrichlorosilan. The membrane was used for direct contact distillation of water containing carbendazim. It showed a flux of 214 g/m^2 h.

4.3 Sintering

Sintering is a technique that is used to synthesize polymeric membranes from powders of polymer or inorganic materials. This technique involves compression and heating of the desired particles below the melting point, stimulating them to stick together. Pores are generated in between the stuck particles which have a size just as the size of the particles. Polymers that can be used for sintering techniques include polyethylene (PE), polypropylene (PP), and polytetrafluoroethylene (PTFE) [43].

Huang et al. [44] electrospun PTFE/poly (tetrafluoroethylene-*co*-hexafluoropropylene) (FEP)/poly (vinyl alcohol) (PVA) ultra-fine fibers on a porous supporting tube. It was subsequently sintered to produce PTFE/FEP porous membranes. The membranes had the potential to separate water–oil emulsions and had a flux of 134 L m^{-2} h^{-1}.

4.4 Phase Inversion

Phase inversion is a versatile technique for preparing polymeric membranes of various pore sizes. In this technique, a polymer soluble in a solvent transform from a fluid state into a solid state under optimized conditions leading to the formation of membranes. Morphology of the prepared membranes depends upon the operating conditions, mostly on the rate of elimination of the solvent and velocity of phase separation. Phase separation can either be non-solvent induced or thermally induced.

Wang et al. [45] synthesized polyethersulfone (PES)/graphene oxide (GO) membranes by using the phase inversion technique and DC electric field. The prepared membrane was used for the elimination of methyl red. It had a high flux of 289.63 Lm^{-2} h^{-1} which is about double the pristine PES. Durmaz et al. [46] fabricated cellulose and cellulose acetate membranes via phase inversion using 1-ethyl-3-methylimidazolium acetate and dimethyl sulfoxide (DMSO). Wet cellulose membranes showed decreased elimination of Bromothymol Blue with an increasing amount of DMSO solvent. On the other hand, dried cellulose membranes showed similar performances in rejection of Blue Dextran and Bromothymol Blue.

4.5 Stretching

This technique is used for making polymeric membranes from semi-crystalline polymers. Pores are produced in the membrane at high temperatures due to stretching perpendicularly to the arrangement of crystallites. The crystallites are arranged in the direction of extrusion.

Li et al. [47] studied and optimized the stretching conditions required for the formation of hollow PTFE membranes. The authors concluded that the membranes synthesized at low stretching temperature and high stretching ratio exhibited high flux and rejection as a result of high porosity and regulated size of pores. Ji et al. [48] prepared poly(vinylidene fluoride) (PVDF) hollow fiber membranes through the process of melt-spinning and stretching. The synthesized membrane was used for the elimination of SiO_2 and active sludge. It exhibited a rejection of 99.99% and lowered turbidity. Table 1 summarizes all the methods that were discussed in the previous sections and their merits and drawbacks.

5 Membrane Antifouling Approaches

For the past few decades, scientists are seeking for developing membranes having potential antifouling properties. Fouling is a major problem arising from various interactions occurring between membrane surface and foulants. The types of interactions happening between foulants and membrane are shown in Fig. 4 [56].

These foulants get attached to the surface of the membranes, as a result, it blocks or narrows down the membrane pores. As a result of which the efficiency of the membranes decreases. In general, the foulants that have less size than the membrane pore tends to narrow the membrane pores either by blocking the pore or by getting adsorbed on the surface of that membrane. Different types of membrane fouling are shown in Fig. 5. However, the particles having larger sizes tend to form the cake layer upon mixing with other particles on the membrane surface [57]. The cake layer is considered as permanent membrane fouling which is very difficult to clean. At present, the target is to design materials having antifouling as well as antibacterial properties to increase the longevity of the membrane. Various materials have been reported to show antifouling characteristics in an application. These are mainly implemented against microbial, organic, and inorganic fouling.

Table 1 Different methods used for membrane preparation and their applications

Technique	Pore size	Application	Merits	Demerits	References
Sintering	0.1–10 µm	Microfiltration	High temperature resistant, chemical resistant	A large amount of material is required, high energy cost, high capital cost	[43, 49]
Track-etching	0.02–10 µm	Ultrafiltration, microfiltration	Controlled pore size, density	Comparatively low porosity, non-uniform surface charge and shape	[40, 50]
Stretching	0.1–3 µm	Microfiltration	High porosity, large scale production, available in commercial modules	Production of thick membranes, restricted to semi-crystalline polymers	[43, 51]
Phase inversion	From dense to few microns	All fields	Versatile membrane structures and thickness, Less compressible	Availability of suitable solvents, environmental hazards	[52, 53]
Electrospinning	From ten nanometer to several micrometers	All fields	High porosity, high surface-to-volume ratio, light weight	Difficult to handle due to charge accumulation, small scale production, salt retention	[54, 55]

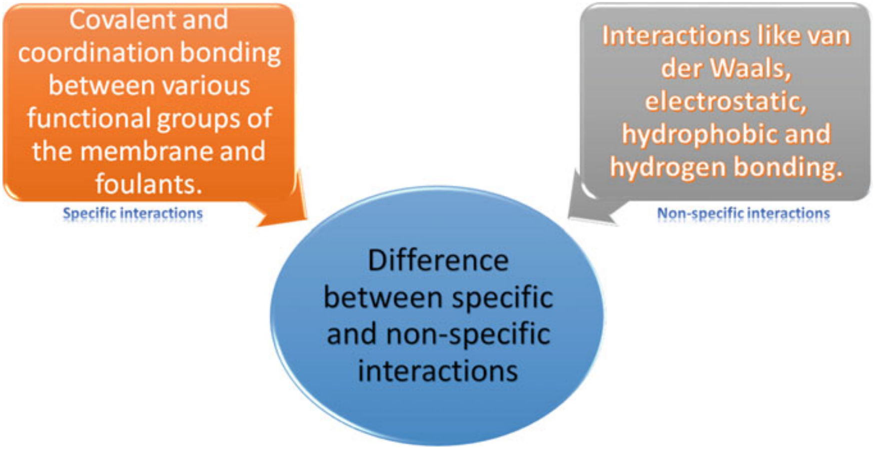

Fig. 4 Basic difference between specific and non-specific interactions

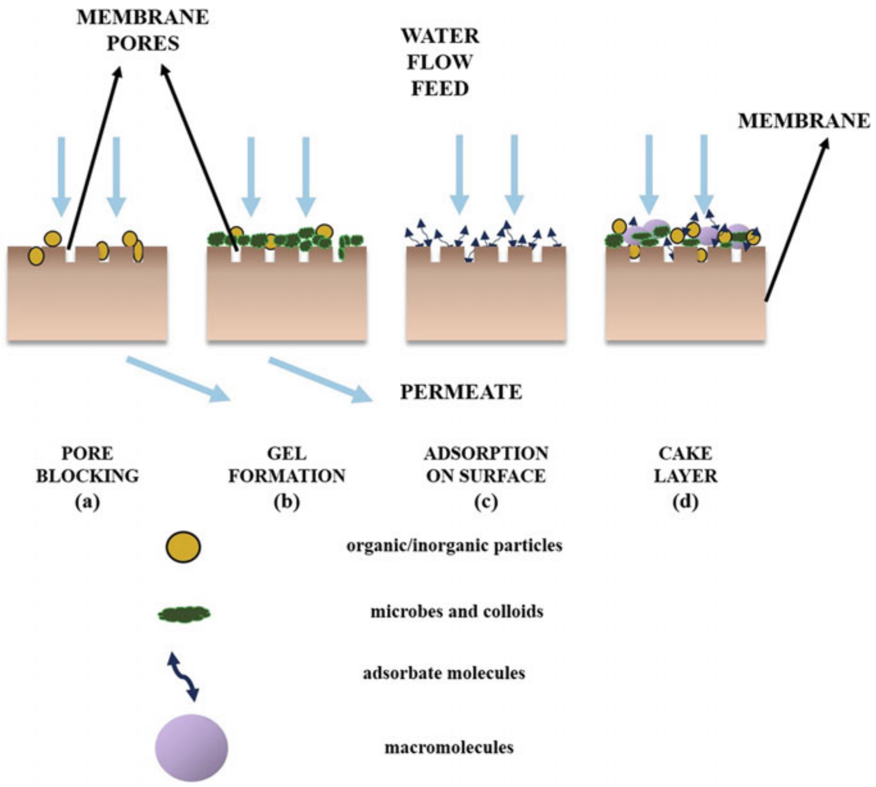

Fig. 5 Types of membrane fouling based on causing agent

5.1 *Microbial Mediated Antifouling*

Fungal, bacterial, and algal growth on the surface deposition the surface of the membrane has a huge impact on its efficiency. As a result of their growth biofilm formation occurs on the membrane surface and ultimately results in membrane fouling [58]. The physical structure of a biofilm is like that of a gel and has slimy and adhesive characteristics, so it is very difficult to clean them off the membrane surface. It has been reported that this biofilm must be detected in the earlier stage as with the cake layer formation the difficulty in removing them increases [59].

To reduce these types of complications various antifouling membranes are being developed to deal with fungal, bacterial, and algal growth. Similar to the work by Shen et al. who created a surface modified TFC membrane, the membrane was developed by surface ionization with various metal ions. It is reported that due to surface modification of the TFC membrane it showed better anti-adhesive and antibacterial properties compared to ordinary TFC membranes. Polyethyleneimine and N-containing organic phosphonic acid in the membrane resulted in better anti-adhesive properties against bovine serum albumin. And silver atoms attached with the membrane provided anti-bacterial properties against S. aureus and E. coli bacteria [60]. Besides the use of metal ions for the prevention of biofilms different photocatalyst materials (TiO_2, ZnO, and CuO) are also used in the membranes for the photocatalytic degradation of bacterial growths [61]. A work by Damodar et al. reported that polymer membranes grafted with TiO_2 show high antibacterial properties against *E. coli*. [62]. Similarly, it has been reported that N-Halamine materials can improve the antibacterial property of the membrane against *Escherichia coli* and *Staphylococcus aureus*. In 2013 by the use of the same material N-Halamine Yu et al. developed SiO_2@N-Halamine Polyethersulfone hybrid membrane which had showed improved antibacterial and organic antifouling properties [63].

This is the antifouling approach utilized to protect the membranes from fouling caused by a fungus, bacteria, and algal growth. But not only by surface modifications but membranes can also be saved from fouling by applications of various cleaning procedures. This includes applying various chemical treatments and washing methods.

5.2 *Inorganic/Organic Antifouling in PMWR*

Inorganic fouling refers to fouling caused by the deposition and blocking of membrane pores by inorganic precipitates like metal hydroxides. Formation of scaling due to change in pH. A list of inorganic fouling causing agents is mentioned in Table 2. However, organic fouling is caused by the accumulation of natural organic matter (NOM), polysaccharides, polyoxyaromatics, proteins, organic dissolved components, etc. [58]. Scale formation is a major cause of inorganic fouling. This mainly happens due to crystallization and particulate fouling. Precipitation of ions on the membrane surface causes crystallization whereas deposition by convective transportation of colloidal particulate matter on the membrane surface causes particulate fouling [64].

Various antifouling approaches are constantly being studied to produce modified membranes (microfiltration, ultrafiltration, nanofiltration, forward osmosis, and reverse osmosis). In this surface modification is an important process to reduce fouling. Some of the methods to modify membrane surface include the use of blends, grafts, coating, etc. There are several reports on this, like surface modification of polyamide membrane by nanoporous titanate nanoparticles for water source having a high quantity of organic, inorganic foulants, and brackish water [65]. In a study, surface modifications were done using a polyelectrolyte coating upon a nanofiltration membrane. With the implementation of such modifications, various surface properties like hydrophilicity and roughness were improved and led to enhanced the antifouling nature [66]. Hydrogel membranes are made of hydrophilic polymers and have a wide range of applications in water treatment, desalination, etc. [67]. Hydrogel membrane can be used to treat high concentrations of organic pollutants present in water bodies. Qin et al. prepared a forward osmosis membrane with an ultrathin hydrogel layer which exhibits high antifouling properties against organic foulants

Table 2 List of common inorganic fouling agents

Inorganic fouling agent	Sources
Cations	Fe^{3+}, Mg^{2+}, Al^{3+}, Ca^{2+}
Anions	$CO_3{}^{2-}$ Source = $CaCO_3$, $MgCO_3$
	F^- Source = FeF_3, AlF_3, CaF_2, MgF_2
	OH^- Source = $Mg(OH)_2$, $Ca(OH)_2$, $Fe(OH)_3$
	$PO_4{}^{3-}$ Source = $Ca_3(PO_4)_2$, $AlPO_4$, $FePO_4$, $Mg_3(PO_4)_2$
	$SO_4{}^{2-}$ Sources = $MgSO_4$, $CaSO_4$
Salts	$Fe(OH)_3$, $FePO_4 \cdot 2H_2O$, $Mg_3(PO_4)_2$, $Al(OH)_3$, $MgCO_3 \cdot 3H_2O$, $AlPO_4$, $Ca_3(PO_4)^2$, $CaSO_4$, $CaCO_3$,

such as protein, oil, humic acid, and alginate. It is reported that this antifouling property of this FO membrane is due to high hydrophilicity and low roughness. As a result of this property, foulants can be easily removed from the membrane surface by simple physical cleaning methods rather than the use of chemical methods of cleaning [68]. The blending method is a simpler process to fabricate new materials. There are several works in which nanoparticles such as carbon nanotube, ZnO, ZrO_2 Al_2O_3 were used to blend with other materials to obtain new membranes [69–71]. It is said in the microbial antifouling section the prepared SiO_2@N-Halamine Polyethersulfone hybrid membrane has organic antifouling and is also able to prevent microbial fouling prepared by blending with SiO_2@N-Halamine using the phase inversion method. As a result of this, the membrane showed both antifouling and antibacterial properties [63].

5.3 *Bio-enzyme Antibacterial Mediated Antifouling*

For the past decade, various bio-enzymes have been targeted for use in membrane modifications. Enzymes are preferred as they are easily biodegradable and thus do not possess a threat to environmental pollution. In a work, Nady et al. presented a membrane with enzyme-catalyzed surface modification. Here the surface of a Polyethersulfone (PES) membrane is modified using phenolic acid (enzyme–substrate). One of the major drawbacks of the PES membrane is fouling due to various proteins. The main purpose of this enzyme surface is to act as a protein repellent and thus act as an antifouling membrane [72]. Membranes used in filtration are generally cleaned using various chemicals. Many enzymes have been reported to be effective in cleaning membranes of foulants with the additional use of other chemicals. Yu et al. found that α-amylase, lipase, cellulase, and protease cannot solely be used to

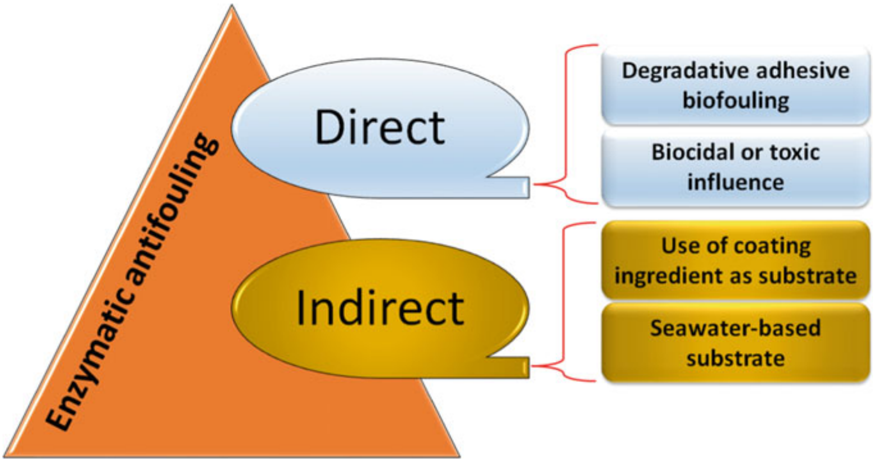

Fig. 6 Categorization of enzymatic antifouling

remove foulants but when used together with other chemicals like Citric acid and NaOH effective cleaning was done [73]. In the present day, researchers are constantly trying to prepare advanced membranes having the self-cleaning ability to minimize the chances of fouling. In a work, pancreatin was covalently immobilized on the PES membrane. It was found that on adjusting pH and temperature (protease, lipase, and amylase) the bio-enzymes present in pancreatin can actively degrade the fouling layer formed on the membrane surface [74]. In general, there are two methods in enzyme-based membrane antifouling (direct and indirect) as shown in Fig. 6. Here the enzyme-based coating is one of the important methods to prevent fouling. In a work, protease enzyme has been used to prepare an antifouling coating on the membrane which can readily prevent fouling due to proteins [75]. Not only in the case of prevention of proteins, but enzyme-based coatings have also proven effective against microbial fouling. The coating containing starch, glucoamylase, and hexose oxidase is able to produce hydrogen peroxide gas enzymatically. As a result of which there has been a significant decrease in the formation of the bacterial biofilm [76]. In another work, Subtilisin is immobilized in maleic anhydride copolymer thin film as an enzyme coating. The enzyme coating was successful in preventing the growth of the green alga Ulva linza and the diatom Navicula perminuta on the membrane surface [77].

5.4 *Surface Roughness Mediated Antifouling PMWR*

By the study of the surface of various membranes, it has been possible to understand the relationship between fouling and roughness of membrane surfaces. For this, surface structure of different membranes is analyzed with the help of atomic force microscopy. This characterization helps to find out how smooth or rough the surface of membranes is.

Multiple research works have confirmed that membrane fouling increases with the roughness of the membrane surface [78, 79]. By the use of the static adhesion test, it has been found that nanosized particles adhere more to the rough membrane surfaces than smooth surfaces [80]. In one of the works, Woo and his research group studied the antifouling property of a microfiltration membrane having a smooth surface and compared it with that of a similar membrane having a rough surface. Both the membranes did have similar pore size distribution and average pore size. But it was found that the final fluxes of the membrane with a smooth surface are about 4.98% higher than that of the membrane with a rough surface [81].

6 Polymeric Membranes for Effluent Treatment in Different Industries

A huge amount of water is required in different industries where various types of contaminants are directly discharged into the water. As a result, contamination of fresh water is a major concern for its significant contribution to the pollution of water. Due to the direct discharge of toxic pollutants in the water, the chemical oxygen demand (COD) is rapidly increasing which causes harmful effects on natural water bodies. The color and odor of water are also changing because of various dyes, hazardous organic and inorganic substances, untreated water, raw materials are continuously mixing with the fresh water in nature. So, to remove the pollutants and reduce the contamination level, the treatment of water is very important. Among various techniques of wastewater treatment membrane technology is very much popular because this technique is very economic and convenient to install and use [82, 83].

6.1 Food Industries

Different types of harmful effluents are generated in various steps of a food industry system. Food production, processing, transportation, and storage are directly or indirectly had an impact on water pollution or any other environmental pollution. Many harmful contaminates from dairy industries, fruit processing industries, meat industries are directly mixed with fresh water. In addition to that, if the discharged industrial water is not treated properly, there is a significant loss of biomass and valuable nutrients [84]. Fruit and vegetable food processing industries contain solid waste such as rinds, seeds, skins from different organic raw materials. Meat, poultry, and seafood industries discharge skeleton waste, animal fat, blood, eviscerated organs into the water. Beverage and fermentation industries wastewater contains various materials

Table 3 Membrane processes used in various industries

Membrane approach	Solutes held	Diameters of retained particles (μm range)	Food industry-based effluents treatment utilization
MF	Bacteria, colloids, grease, fats, organic microparticles, oil, etc.	10^{-1} to 10	Beverage, cereal, diary, oil, etc.
UF	Oils, pigments, proteins, sugar, etc.	10^{-3} to 1	Beer, cereal, diary, fish, meat, oil, vegetables, wine, etc.
NF	Divalent cations and anions, lactose, sulfates, pigments, sodium chloride, sucrose, etc.	10^{-3} to 10^{-2}	Beverage, diary, meat canning, olive oil, etc.
RO	Inorganic ions, salts, etc.	10^{-4} to 10^{-3}	Fish, diary, meat, vegetables

used in the fermentation process. Waste streams of dairy industries contain waste milk which eventually degrades to form lactic and formic acids [82].

Membrane technology can be used to remove pollutants from food processing industrial wastewater. Depending upon the pollutant materials microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) techniques can be applied. After removing the contaminants from wastewater, the fresh water and removed compounds can be recycled once again which can reduce the cost of processing and water consumption [85]. The application of various membranes to various food industries is shown in Table 3.

6.2 *Pharmaceutical Industries*

Nowadays health protection is a major concern due to the rapid increase of diseases all over the world. In the past few years, rapid industrialization of pharmaceutical manufacturing industries led to the rapid development of the country, but a concurrently huge amount of water pollution also occurred for this reason. Recently, the pharmaceutical industries are among the top five industries in the global economy in addition to that it is one of the major sources of water pollution. A large amount of water is required for various processes in these industries such as production, processing, formulation, cooling, etc. These numerous processes generate a large amount of wastewater in which a high concentration of toxic, organic, and inorganic compounds are present. This wastewater contains steroids, hormones, drugs, antibiotics, lipid regulators which can harm various water bodies and the overall environment. The COD (chemical oxygen demand) of pharmaceutical wastewater is very high which can disturb the ecological balance. Much attention should be paid to removing these pollutants so that we can reutilize the wastewater and reduce the health hazard by eliminating the pharmaceutical contaminates [86]. Different major pollutants from various pharmaceutical industries and their BOD and COD have been shown in Table 4.

Traditional methods are unable to eliminate all the pharmaceutical pollutants so, membrane technologies can be a very good alternative that can erase contaminates from water. But individual technology can't remove all compounds, so membrane technology can be combined with conventional technology and by this hybrid process pollutants can be removed efficiently and economically. Depending upon the pore size, membrane composition, driving force, and membrane composition, different types of the membrane can be used such as MF, UF, NF, RO membrane, etc. [95]. The pore size of MF and UF is greater than the size of contaminants for this reason these membranes are not frequently used. NF and RO membranes are used for this purpose which have low pore size [96]. NF/RO membranes are extensively used for

Table 4 Major pollutants from different pharmaceutical industries and their BOD and COD

Pharmaceutical industry	COD (mg/l)	BOD (mg/l)	Major pollutants (mg/l)	References
Antibiotic producing industry	12,500 ± 1070	9400 ± 980	Butyl acetate 1500 ± 350 Methylene chloride 500 ± 98	[87]
Herbal pharmaceutical industry	5000 ± 80,000	–	Lignin 450 ± 8500	[88]
Chemical synthesis pharmaceutical industry	40,000 ± 60,000	–	–	[89]
Bulk drug pharmaceutical industry	13,000–15,000	7000–7500	Antipyrene 5–10 Carbamazepine 10–15 1-bromonapthalene 5–10 dibutyl phthalate 30–40	[90]
Bulk drug manufacturing industry	34,400 ± 2000	22,000 ± 1200	–	[91]
Antibiotics waste from manufacturing and equipment cleaning industry	16,547 ± 1827	10,184 ± 2574	Triethylamine 9872 ± 2142	[92]
Antibiotic waste	34,348 ± 1425	–	–	[93]
Chemical synthesis pharmaceutical industry	20,000–230,000	–	Etodolac 50–215	[94]

the removal of antibiotics from waste water [96]. For the last two decades, membrane bioreactors are used extensively because it is economically beneficial and it has immense sludge retention time (SRT) [97].

6.3 Textile Industries

Textile industries are considered as one of the largest industries worldwide. The growth of textile industries caused some accidental effects on the environment and water pollution is most significant among them. Textile industries require a huge amount of fresh water as a result various contaminants are directly discharged into this. It is reported that if textile industrial wastewater is not treated properly, it can cause serious environmental issues. The untreated or incompletely treated wastewater can be very harmful to water bodies and terrestrial life. Various types of organic compounds, heavy metals, inorganic salts are used in textile industries and dyes are considered as a major contaminant among them. The pollutants related to these industries decrease oxygen concentration and block the water permeability through the water which totally imbalance the water ecosystem [98]. It has high COD, low BOD/COD ratio, high total dissolved solids (TDS), high pH, high turbidity, and high salinity [99]. In Table 5 characteristic of wastewater which is taken from various steps of the textile industry is shown in detail.

Membrane technologies are extensively used for textile wastewater treatment. Mechanical, chemical resistance, thermal stability, pore size, materials are basic parameters to select a membrane that can give maximum removal percentage and have minimum fouling behavior. Membrane technologies are advantageous because the toxic chemicals can be recovered and reuse of these can reduce the cost of processing [82]. The microfiltration technique is often used for the removal of colloidal and suspended dye particles from water, but this technique can't be used as an independent technique to erase all the effluents because toxic compounds and complexes are not removed by the MF membrane. UF membranes are rarely used for these types of water treatment because the molecular weight of the dye complexes is much lower than the molecular cutoff of the UF membrane, but it can be used as a pretreatment before carrying the water to other membrane techniques. We can get a very good quality of treated water by using the nanofiltration membrane and NF membranes are very advantageous because they have high solvent permeability, are convenient to use and have good chemical cleaning capability which suggests that they can be used as a mainstream technique for textile waste water treatment [101]. RO membranes are used for recovering macromolecules and ionic compounds from textile industrial waste water [102]. Various kinds of integrated or hybrid processes are also used to minimize the contamination level of textile wastewater [103].

Table 5 Characteristics of textile wastewater obtained from different stages of textile processing. Reprinted with permission from Dasgupta et al. [100]. Elsevier

Characteristics	Scouring	Bleaching	Mercerising	Dyeing	Composite	Discharge limit into public sewage Bureau of Indian Standards (BIS-3306–1955)	Maximum permissible limit for water reuse
pH	9–14	8.5–11	8–10	1.5–10	1.9–13	5.5–9.0	6.5–9.2
TDS (mg/L)	12,000–30,000	2500–11,000	2000–2600	1500–4000	2900–10,000	2100	–
TSS (mg/L)	1000–2000	200–400	600–1900	50–350	100–700	100	–
Color	–	–	Highly colored	Strongly colored	Strongly colored (>14,000 Pt–Co units)	Colorless	Colorless
BOD (mg/L)	2500–3500	100–500	50–120	100–400	50–550	30	–
COD (mg/L)	10,000–20,000	1200–1600	250–400	400–1400	250–8000	250–500	–
Chlorides (mg/L)	–	–	350–700	–	100–500	600–1000	600
Sulphates (mg/L)			100–350		50–300	1000	400

6.4 Leather Industries

Tannery industries are one of the oldest and largest industries that have huge potential for employment, growth, and exports to foreign countries [104]. Different types of goods are produced in those industries such as leather garments, footwear, and leather accessories like bags, wallets, belts and among them, footwear is most important as it consumes more than half of total leather production [105]. But these industries release a huge amount of hazardous compounds which direct mix with fresh water. These effluents from leather industries are classified as a critical environmental hazard because of the high toxicity of the substances which include inorganic and organic dissolved matters, sulfide, chromium, lead ions and other heavy metals, chlorine, ammonia, and other various pollutants [82]. These pollutants can cause skin cancer, ulcer, and other critical diseases which have a high mortality rate. Various characters of textile/leather industry wastewater vary with every step of leather manufacturing, and it is shown in Table 6. In Table 7, various contaminating hazardous metals and their percentage are shown.

Treatment of these effluents is very important to save the ecosystem and the overall environment. Various techniques such as adsorption, coagulation, flotation, electrochemical processes are available but membrane technology is a wildly accepted and popular technique for the treatment of leather industrial, and tannery waste water because of its high efficiency, low cost, and eco-friendliness [82]. MF, UF, NF, RO techniques are used independently or in an integrated hybrid process. Depending upon contaminations which membrane can be used is determined. Tannery industry wastewater treatment contains three steps, first is primary or chemical-physical treatment in which sedimentation, sludge separation occurs. The second step is secondary or biological treatment in which recycling of sludges and their separation take place. And the final step is tertiary treatment and in this step filtration, redox processes are done [106]. Biological treatment is done by UF membrane which is coupled with a bioreactor. RO membranes are also used to reduce the salt content of wastewater. Besides these techniques hybrid membrane processes are used in which a conventional technique is combined with a membrane technique or a membrane technique is coupled with other membrane techniques.

6.5 Petroleum Industries

Different sections of petroleum industries include natural gas production, production of gas to a liquid, liquefied natural gas, and production of oils. These production units consume a huge amount of fresh water and discharge wastewater which contains various effluents. The waste water is produced either during the production of hydrocarbon which is a result of oil and gas dispersion or when it is applied at different components to control the process such as cooling or oil processing [106]. The wastewater of petroleum industries mainly contains oil, grease, organic matters

Table 6 Characteristic of leather industry wastewater at various steps of processing (Mean composition and volume percentage of various wet operations in a leather industry). Reprinted with permission from Cassano et al. [106]. Elsevier

Parameters	Soaking		Liming		Deliming-bating		Pickling	Chromium tanning	Dyeing, fat liquoring, retanning		Other effluents
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
pH	6	10	12.5	13	6	11	4	3.2	4	10	–
Temperature (°C)	10	30	10	25	20	35	–	–	20	60	–
Sedimentable materials (mg/l)	100	250	300	700	50	150	20	45	100	500	–
Total suspended solids (mg/l)	2300	6700	6700	25,000	2500	10,000	380	1400	10,000	20,000	–
BOD_5 (mg/l)	2000	5000	5000	20,000	1000	4000	100	250	6000	15,000	–
COD (mg/l)	5000	11,800	20,000	40,000	2500	7000	800	400	15,000	75,000	–
Chromium(III) mg/l	–	–	–	–	–	–	–	4100	0	3000	–
Sulfides (mg/l)	0	700	2000	3300	25	250	–	–	–	–	–
Chlorides (mg/l)	17,000	50,000	3300	25,000	2500	15,000	8950	2000	5000	10,000	–
Oils and fats (mg/l)	1700	8400	1700	8300	0	5	–	–	20,000	50,000	–
Chlorinated solvents (mg/l)	–	–	–	–	0	2500	–	–	0	250	–
Surfactants (mg/l)	0	400	0	300	0	500	–	–	500	2000	–
Discharge water on total volume (%)	18		12		22		2	3	38		5

Table 7 Elements present in a leather industry wastewater and their approximate percentage

Sl. No.	Element	Proportion (%)
1	Ca	62.46
2	Si	9.770
3	Fe	8.851
4	Cr	6.770
5	Mg	3.730
6	Al	2.800
7	S	2.110
8	Ti	0.808
9	K	0.455
10	P	0.444
11	Sr	0.161
12	Cu	0.083

like hydrocarbons such as paraffin (methane, ethane, propane), naphthene (dimethyl cyclopentane, cyclohexane), aromatics such as benzene, toluene, xylene, etc. and naphthenic acids that are also present at significant amounts [107, 108]. Petroleum industry wastewater is rich in organic pollutants and oil. So, it is difficult to treat this water and remove all the effluents [109]. The chemical characteristics of produced water in a gas and oil field are shown in Table 8.

MF membranes are used as a pretreatment process to increase the effectiveness of UF, NF, or RO techniques. Oil removal can be done by using the UF process along with the MF process, but one disadvantage of this process is that UF membranes are very susceptible to fouling. So, to overcome this problem the membrane surfaces are made hydrophilic, and the surface roughness is reduced. NF and RO membranes are used for this water treatment purpose [110].

Table 8 Typical chemical characteristics of produced water. Reproduced with permission from [110]. Copyright Adham et al. [110] Elsevier

Parameter	Oil field [111, 112]	Gas field [113]	SAGD [114]	Coal bed methane field [115]
TDS, mg/L	247,000	5200	<10,000	2510
Sodium, mg/L	69,160	1030	3000	1350
Chloride, mg/L	152,750	2300	4800	62
TOC, mg/L	500–2000	500	430	2
HCO_3, mg/L	310	–	1400	1700
pH	5.6	4.3	8.8	8.4

7 Challenges and Outlook

According to reports, most nations have environmental legislation limiting oil concentration in final wastewater discharge to 10–15 mg/L [116]. Membrane fouling reduces the membrane's lifespan as well as its performance in terms of water flow, permeability, and oil rejection. Membranes with a high hydrophilic property are advantageous for treating greasy wastewater. Most earlier research used hydrophilic membranes rather than hydrophobic membranes because this encourages high water flow performance. Furthermore, the hydrophobic membrane has a significant oleophilic leaning property [116]. Both the hydrophobic and oleophilic wetting qualities of the membranes reject water molecules while allowing oil molecules to flow through, resulting in oil fouling on and inside the pores. Permeation occurs when oil droplets pass through a porous medium.

This layer cake creation causes membrane obstruction, which reduces membrane permeation performance and eventually prevents water molecules from passing across the membrane. Apart from oil molecules, oily wastewater also contains other contaminants such as protein. This impurity may contribute to a higher likelihood of membrane fouling.

Because of the intricacy of the materials used in MMM manufacturing, the presence of inorganic nanoparticles as addition may provide a challenge. This issue hampered the creation of a homogeneous dope solution and resulted in the aggregation of additives.

In the structure of the membrane, because there is a barrier obstructing the water molecules from smoothly passing across the membrane, agglomeration would lower the effective contact area and water flow performance.

According to Garca-Ivars et al., the size and shape of the nanoparticles play an essential impact on their wetting capabilities and dispersion. Nanoparticles less than 100 nm have a harder time settling in dope solutions than macroparticles [117]. Spherical nanomaterials, on the other hand, are preferred over polyhedral nanoparticles because they have fewer contact points between particles, which prevent agglomeration and aggregation. Aside from that, nanoparticle agglomeration may only result in nanoparticle leakage, since the nanoparticles prefer to permeate alongside the feed permeation.

The creation of membranes formed from expensive materials such as PAN and nanoparticles, from an economic standpoint, remains a hurdle to their practical deployment. As a result, using low-cost materials and a basic procedure is a possibility.

Furthermore, carbon-based compounds such as carbon nanotubes (CNTs) and graphene are among the most widely used materials because they improve membrane hydrophilicity and oleophobicity. Aside from material selection, there are a number of other aspects to consider when calculating total operating and maintenance costs for the entire membrane treatment process. Membrane replacement, chemical, energy, labor, and so on, as well as maintenance, should all be considered. According to

Ersahin et al., the membrane system's significant contribution is endowed by chemical consumption, labor service, and energy consumption, which accounted for 35, 22, and 17% of the overall expenses, respectively [118]. Reduce the number of membrane cleanings to reduce chemical use.

It is not, however, impossible to design and manufacture lab-scale membranes for industrial uses. It is critical to have a thorough grasp of chemical compositions and reactions in order to build membranes with the desired properties. As a result, more work will be necessary to develop high-quality membranes comparable to current technology.

8 Conclusion

Membrane biofouling is one of the most significant challenges to membrane-based separation's long-term durability. As a result, in membrane technology for water and wastewater treatment, the development of anti-biofouling expertise is critical. Early initiatives focused on developing hydrophilic membranes with anti-adhesion properties to reduce surface biofouling. However, due to continual bio-adsorption, development, and regeneration of bacteria on polymer membranes, this is insufficient to manage biofouling over a long-term operation.

Current research is beginning to focus on the construction of antibacterial membranes by combining and surface functionalizing biocidal nanoparticles with polymers. Various antibacterial agents, including inorganic, organic, and enzymatic-based compounds, have been used for membrane functionalization to achieve this goal, with promising results.

In general, metal-based nanoparticles and carbon-based nanomaterials are regarded as potential options for inorganic biocides due to their strong antibacterial efficacy, high stability, and commercial availability. Furthermore, such materials can provide membranes with other desirable features such as a smooth, hydrophilic surface, resulting in increased membrane fouling resistance.

Nonetheless, the inorganic filler's poor compatibility with the organic membrane remains a technical challenge. It is hypothesized that organically decorated inorganic nanoparticles improve interface adhesion within polymeric matrices, which also applies to membranes with a thin polymer-based active layer.

Despite the strong antibacterial activity provided by these nanomaterials, issues such as the release of (heavy) metal ions that cannot be rejected by membranes and nanomaterial leaking from antibacterial membranes remain.

This must be thoroughly investigated when employing multifunctional nanomaterials to make antibacterial changes. Furthermore, future studies should focus on good control of the release rate, with the goal of successfully inactivating bacteria strains and extending the validity time. Due to the limited lifespan of antibiofouling capabilities, which is closely linked to the slow dissolution of biocides from membranes, using antibacterial membranes in realistic operational settings is still a big difficulty. To improve the antibacterial durability of the modified membranes, significant efforts should be made to build long-lasting antibacterial membranes. The practical application of these antimicrobial membranes in real-world situations needs to be investigated further. In this context, tracking the detection of released antibacterial agents is useful for better understanding antibacterial efficacy and resistance.

Surface modification and immobilization of NPs onto larger-size supports are currently being used to control the release profile of biocides as well as boost metallic nanoparticles' stability within the membrane matrix. Furthermore, the size and morphology of inorganic biocides can be tweaked to improve the membranes' overall effectiveness.

Advanced organics with specific chemical structures have evolved as new antimicrobial ingredients for membrane modification, in addition to inorganic antibacterial NPs. Although the inclusion of organic bacterial agents into the polymeric membrane is conceivable, the membrane's operational stability, particularly towards membrane disinfectant, remains a difficulty.

Surface grafting by polymerization is a promising method for firmly anchoring organic biocides to membrane surfaces against bacterial activation.

However, the high cost and stringent laboratory conditions play a big role in deciding whether or not to use organic compounds as a bactericidal agent. Biocatalysts antimicrobial agents, on the other hand, provide a safe, effective, and environmentally friendly way to control microbial activity on membrane surfaces. However, due to a dearth of inexpensive enzymes and the instability of free enzymatic reactions, this area of research is still in its early stages. As a result, current research is focused on using cutting-edge enzyme immobilization techniques, such as metal–organic framework encapsulation, to enhance the stability and recyclability of enzymes.

As antibacterial surface design advances, a smart antibacterial surface technique based on 'death release' cleverly merges the dual functions of antibacterial and antimicrobial surfaces.

In comparison to typical antibiofouling surfaces with a single purpose, such as antiadhesion or bactericidal capabilities, this proposed new technique has advanced rapidly in the previous five years. For the design of smart antimicrobial surfaces, function switching that is controlled by internal or external stimuli is critical. These principles and methodologies are promising for designing the antibacterial surface of polymeric membranes, aiming for a robust and long-term antibiofouling performance, despite the fact that such smart antibacterial surfaces are only widely used in clinical applications.

Despite significant advances, there are still a number of unresolved concerns with antimicrobial membranes. The following are some of the issues that need to be addressed. (1) To date, most antibacterial changes have been limited to a lab scale.

Because of the rigorous preparation conditions and high cost of nanomaterial functionalization, scaling up modification procedures is difficult. Furthermore, research on the actual usage of antibacterial membranes in realistic situations has been rare, implying that there are still some information gaps to fill in order to produce nanocomposite antibacterial membranes for industrial water treatment. (2) Membrane antibacterial activity assay: Because most current researchers continue to employ a static antibacterial assay approach based on traditional antibacterial agent tests, the results may fail to predict antibacterial membrane performance in a real-world dynamic water filtration process. (3) Membrane filtration behavior: antibacterial drugs can be added to improve bacterial resistance. This, however, may affect membrane filtering performance such as water flux, salt rejection, and operational stability.

To preserve or improve membrane filtration performance following antibacterial treatment, a lot of effort should be put into controlling the membrane structure. (4) Antibiofouling membranes: the actual relationship between membrane biofouling and bacterial fouling in long-term operation is yet unknown. Despite the fact that the connected bacteria are inactivated by the antibacterial membrane, the released intracellular material may supply appropriate substrates for subsequent bacterial colonization, resulting in severe membrane fouling. We believe that the creation of an anti-fouling membrane with an antibacterial function will accelerate the development of antibacterial membranes and, in turn, lead to the development of a high-efficiency anti-biofouling membrane for water treatment.

Acknowledgements The authors wish to appreciate the Centre for Research in Nanoscience and Nanotechnology, and the Department of Polymer Science and Technology University of Calcutta for their financial and technical support.

Declaration All authors have contributed equally to the writing of this book chapter.

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